

Dynamical Crossover in Supercritical Core-Softened Fluids

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(Dated: July 15, 2015)

It is well known that some liquids can demonstrate anomalous behavior. Interestingly, this behavior can be qualitatively reproduced with simple core-softened isotropic pair-potential systems. Although anomalous properties of liquids usually take place at low and moderate temperatures it was recently recognized that many important phenomena can appear in supercritical fluids. However, no studies of supercritical behavior of core-softened fluids is reported. This paper reports a study of dynamical crossover in supercritical core-softened systems. The crossover line is calculated from three different criteria and good agreement between them is observed. It is found that the behavior of the dynamical crossover line of core-softened systems is quite complex due to its quasi-binary nature.

PACS numbers: 61.20.Gy, 61.20.Ne, 64.60.Kw

The most fundamental approach to the behavior of matter relies on the interactions between the particles of the substance. One can use an approach based on quantum mechanical treatment of interactions which is the most accurate one. However, such ab-initio methods require a lot of computational resources and cannot be applied to the systems larger than several hundreds of atoms. A great advantage was made by application of so called effective potentials. These potentials are constructed in such a way that they allow to obtain some principal properties of interest with much smaller efforts. In the simplest case the interaction energy is approximated by pair interactions only. Among the most studied in the literature is Lennard-Jones (LJ) system which has the potential $U(r) = \varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right)$. This system demonstrates a generic view of phase diagram of a substance containing gas, liquid and crystal phases and well describes the behavior of noble gases and some molecular substances.

In our recent works it was shown that supercritical region of the phase diagram can be divided into two parts: rigid liquid and dense gas [1–3]. These regions differ by the microscopic dynamics of particles and are separated by a crossover line called Frenkel line. Later on the phenomenon of dynamical crossover was studied for a number of other fluids [4–8].

Another topic attracting wide attention of researchers is related to anomalous behavior of liquids (see, for example, [9] for the list of anomalies of water). It was found that models with isotropic pair core-softened potentials can demonstrate anomalous behavior [10–17]. Diffusion, density and structural anomalies are widely discussed in the literature [18]. Such systems can also demonstrate numerous structural phase transitions in solid region. This kind of behavior cannot be obtained in systems like LJ. These observations allow to suppose that the behavior of the Frenkel line can also be more complex in the systems with core-softened potentials.

A particular form of core-softened system studied in our previous works is characterized by the following interaction potential:

$$U(r)/\varepsilon = \left(\frac{d}{r} \right)^n + \lambda_0 - \lambda_1 th(k_1[r - \sigma_1]) + \lambda_2 th(k_2[r - \sigma_2]), \quad (1)$$

where d and ε set the length and energy scales and λ_i and σ_i are varied. A large set of parameters was considered. It was found that the phase diagram and anomalous behavior of the system strongly depend on the potential parameters. An important feature of this system is that it demonstrates quasi-binary behavior, i.e. some features commonly observed in binary mixtures [10]. For example, the system can be easily vitrified [10, 19]. The phase diagram of the system consists of low density close packed FCC phase, high density FCC phase and a set of intermediate structures which can be considered as close packing of the particles at large length scale σ_1 , close packed structure at small length scale d and a set of different structures in the region where the competition between these length scales takes place. Obviously, the interplay between two length scales affects the liquid properties too. Therefore it is of interest to monitor the phenomena of dynamical crossover in fluid for such a system.

The system with potential (1) reproduces many unusual properties: complex phase diagram with maximum on

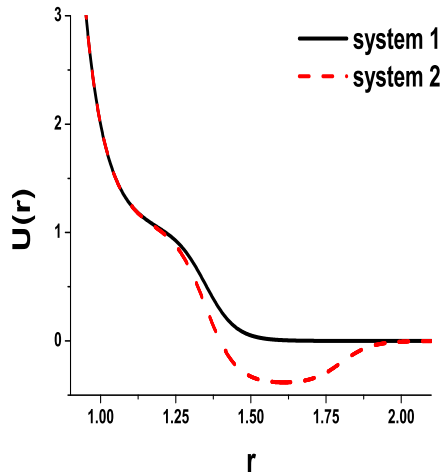


FIG. 1: (Color online) Interaction potentials studied in the present work (eq. (1)).

System number	σ_1	σ_2	λ_0	λ_1	λ_2
1	1.35	0	0.5	0.5	0
2	1.35	1.8	0.5	0.7	0.2

TABLE I: Parameters of the potential (1) used in the study.

the melting line and many different solid phases, anomalous density, diffusivity and structure etc. Basing on this observation we believe that investigation of the dynamical crossover in this system will be helpful for understanding of the behavior of supercritical water and other anomalous fluids.

Two sets of parameter of the potential (1) were studied: a purely repulsive system with the shoulder width $\sigma_1 = 1.35$ and a system with repulsive shoulder and attractive well. The parameters of the potentials are given in Table I. Later on we refer the systems with different parameters as "system 1" and "system 2". The potentials are shown in Fig. 1.

We measure all properties of the system in reduced units with respect to d and ε : $\tilde{\rho} = N/V \cdot d^3$, $\tilde{T} = T/(k_B \cdot \varepsilon)$ and so on. Since only these reduced units are used in the paper, we omit the tilde marks.

In all cases systems of 1000 particles in a cubic box with periodic boundaries were simulated by molecular dynamics method. The timestep was set to 0.0005 reduced units of time. The system was equilibrated by $3.5 \cdot 10^5$ followed by more $1.5 \cdot 10^5$ step for data collection. During the equilibration run the temperature was held fixed by Nose-Hoover thermostat. The propagation run was made in NVE ensemble. All simulations were performed with lammmps simulation package [20].

Several criteria can be used to locate the line of dynamical crossover [1–3]. Among the most convenient ones are the velocity autocorrelation function (vacf) criterion and the isochoric heat capacity one [3].

Vacfs are defined as $Z(t) = \frac{1}{3N} \langle \sum \frac{\mathbf{V}_i(t) \cdot \mathbf{V}_i(0)}{V_i(0)^2} \rangle$ where $\mathbf{V}_i(t)$ is an i -th particle velocity at time t . Vacfs of rigid fluids demonstrate oscillatory behavior whilst vacfs of dense gas decay monotonically. Therefore the Frenkel line corresponds to the (ρ, T) points where the oscillations vanish [3].

The isochoric heat capacity criterion states that at the Frenkel line $c_v = 2k_B$ where c_v is heat capacity per particle. It is based on the counting of contribution to the heat capacity of liquid from longitudinal and transverse excitations. A detailed theory of liquid heat capacity based on excitation spectra was proposed in recent works [21–23]. One can show that in rigid regime the contribution to the heat capacity from the potential energy of transverse modes is $1 \cdot k_B$ per particle. At the Frenkel line transverse excitations disappear and therefore the heat capacity per particle at Frenkel line should be close to $2k_B$.

The crossover between different regimes of fluid also can be observed by appearance of strong positive sound dispersion (PSD). PSD means that the speed of excitations in liquids at some finite wavelength k exceeds the adiabatic speed of sound c_s . PSD was experimentally observed in a number of low-temperature fluids (see, for example, review [24–26] and references therein). As the temperature increases PSD disappears. Previously we considered PSD in Lennard-Jones and soft spheres systems [3] and found that in both cases the temperature of PSD loss is consistent

with Frenkel temperature from vacf and $c_v = 2k_B$ criteria. The PSD disappearance is indeed related to changes of excitation spectrum which take place at the Frenkel line [3]. Therefore it looks reasonable to relate the disappearance of PSD with the crossing of the Frenkel line.

To check the presence or absence of PSD we compute the longitudinal autocorrelation function of the velocity current function:

$$C_L(k, t) = \frac{k^2}{N} < J_z(\mathbf{k}, t) \cdot J_z(-\mathbf{k}, t) >, \quad (2)$$

where

$$J(\mathbf{k}, t) = \sum_{j=1}^N \mathbf{v}_j e^{-i\mathbf{k}\mathbf{r}_j(t)}. \quad (3)$$

After calculation of $C_L(\mathbf{k}, t)$ we evaluated its Fourier transform $\tilde{C}_L(\mathbf{k}, \omega)$. The frequency of the excitations at wave vector \mathbf{k} is given by the location of the maximum of $\tilde{C}_L(\mathbf{k}, \omega)$.

Adiabatic speed of sound is calculated directly from simulations.

In the present work we calculate the Frenkel line from vacf, $c_v = 2k_B$ and PSD criteria for the system 1 and from vacf and $c_v = 2k_B$ criteria for the system 2.

Let us consider the Frenkel line of the system 1. We start with calculation of the points where $c_v = 2k_B$. The location of these points in the phase diagram is shown in Fig. 2.

We proceed the study with calculation of the vacfs of the system 1. Fig. 3 shows the evolution of vacfs of the system at density $\rho = 0.65$ as a function of temperature. One can see strong oscillations at the lowest temperature. However, these oscillations quickly decrease with temperature and disappear at $T = 0.61$. Interestingly, on further temperature increase the oscillations of vacf appear again and disappear for the second time at $T = 1.45$. The points where vacfs lose their oscillations are shown in Fig. 2.

This kind of reversible oscillation behavior of vacf is reported for the first time. One can relate it to the quasibinary nature of the system [10]. The potential of the system 1 contains two length scales: d and σ_1 . Such systems behave qualitatively different at low and high temperature [10]. Since the potential is purely repulsive it is energetically advantageous for the particles to stay far from each other. Therefore at low temperatures and densities the behavior of the system is defined by the parameter σ_1 . If the density and temperature increase the particles penetrate through the soft core and the system behaves more likely as defined by the small length scale d . Apparently, an intermediate region appears in between in which the influence of both length scales is comparable and therefore competition between local structures takes place. This quasi-binary nature is obviously responsible for the complex behavior of the vacfs of the system.

Fig. 4 (a) and (b) show the dispersion curves for the system 1 at density $\rho = 0.8$ and two temperatures - below and above the Frenkel line obtained by vacfs and heat capacity criteria. At low temperature $T = 0.4$ a clear positive dispersion is observed. If the temperature is increased the excitation frequencies approach the line $c_s \cdot k$. Finally the PSD disappears. However, the point of PSD loss is rather difficult to be detected because it becomes close to the level of computational errors.

Like in the case of vacfs we observe some kind of reversible behavior of PSD. There is a density region where if the fluid is heated isochorically PSD disappears then appears again and disappears for the second time at higher temperatures. In case of density $\rho = 0.8$ the temperature of the first PSD loss is $T_1 = 1.6$ and the second one is $T_2 = 2.2$. Indeed, the errors in PSD calculations are quite large and one can relate the second PSD appearance to the computational uncertainties. However, taking into account complex behavior of vacfs one can suppose that PSD also demonstrate sophisticated behavior. Moreover, one can note that two branches of PSD loss at low densities correspond to two effects on vacfs. The lower temperature branch is consistent with the loss of oscillations of vacfs. Apparently at the temperatures of the second branch of PSD loss vacfs are monotonous both at lower and higher temperatures, however, non-monotonous behavior of intensity of vacfs is observed, i.e. the curve of vacf for $T = 2.8$ is located below the one for $T = 3.0$ but above the curve for $T = 3.2$ (see Fig. 5).

Frenkel lines of the system 1 obtained from all three criteria are summarized in Fig. 2. One can see that at the high density regime ($\rho > 0.75$) all three curves perfectly match. In our previous publication the same match was found for Lennard-Jones and soft spheres systems [3]. The high density regime corresponds to the major role of the d length scale, i.e. $(\frac{d}{r})^n$ term of the potential. Therefore this result looks to be consistent with our previous works.

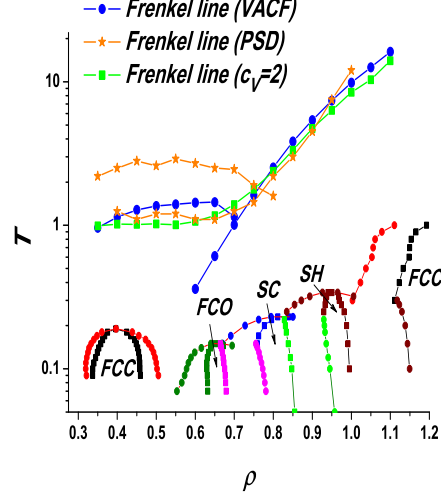


FIG. 2: (Color online) Frenkel line of the system 1 computed from vacfs, $c_V = 2k_B$ and PSD criteria placed in the phase diagram.

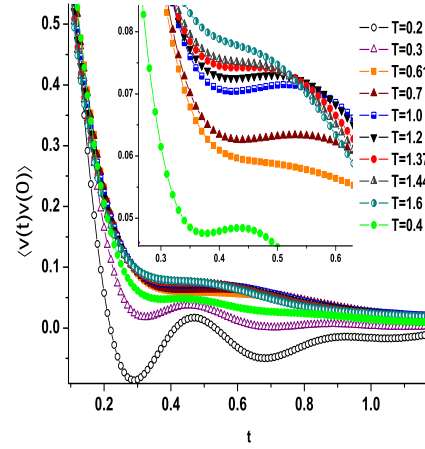


FIG. 3: (Color online) Vacfs of system 1 at density $\rho = 0.65$ and a set of temperatures. The inset enlarges the region where the loss of oscillatory behavior takes place.

At low densities the situation is more sophisticated. One can see that the curves from $c_V = 2k_B$, the first loss of PSD and disappearance of oscillations of vacfs are located close to each other and can be considered as matching. However, the second temperature of PSD loss is substantially higher than all these lines. Moreover, in the region where vacfs demonstrate two points of loss of oscillations the second branch of the lines from vacfs is located below the common curve from three criteria.

From the discussion above one can see that in a purely repulsive core-softened system the Frenkel line behavior becomes very complicated. It is interesting to analyze the behavior of the Frenkel line for the systems with both repulsive and attractive parts of the potential. System 2 is an example of a core-softened system with both repulsive and attractive forces. The Frenkel lines of the system 2 from vacf and $c_V = 2k_B$ criteria are shown in Fig. 6. One can see that like in the case of system 1 the lines from vacf criterion split into two branches. At low densities the upper branch of the line from vacfs is in good coincidence with the line from c_V . At higher densities all lines merge. One can conclude from this picture that the attractive part of the potential does not change the qualitative behavior of the Frenkel line.

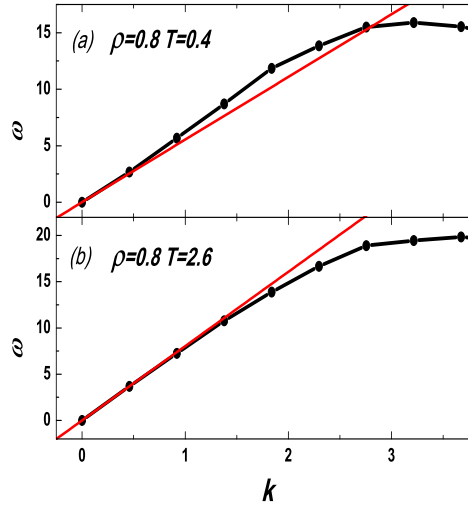


FIG. 4: (Color online) Spectra of longitudinal excitations in system 1 at $\rho = 0.8$ and (a) $T = 0.4$ and (b) $T = 2.6$. The straight lines are $c_s \cdot k$, where c_s is adiabatic speed of sound.

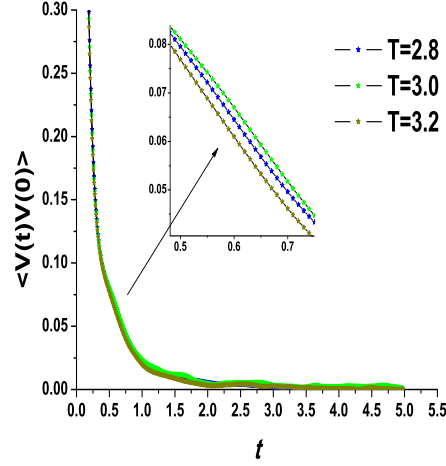


FIG. 5: (Color online) Vacfs of the system in the vicinity of the high temperature branch of PSD loss at $\rho = 0.55$. The PSD disappears at this density at $T = 3.0$.

In conclusion, we report a detailed study of dynamical crossover line in supercritical regime of core-softened fluids. We use three criteria - vacfs, c_V and PSD ones and we find good agreement between them. At low densities the Frenkel line is flat: the temperature is almost independent on density, while at higher densities it rapidly grows up. Similar behavior was recently observed for the Frenkel line of water [6]. Besides we observe that the crossover lines from vacfs and PSD split into two pseudo branches at low densities. The phenomena of the appearance of the additional branches of the Frenkel line is not observed in simple systems and is caused by quasi-binary nature of the core-softened fluids.

Eu. G. thanks the Joint Supercomputing Center of Russian Academy of Science and Yu. F. thanks the Russian Scientific Center at Kurchatov Institute and for computational facilities. The work was supported by Russian Science Foundation (Grant No 14-22-00093).

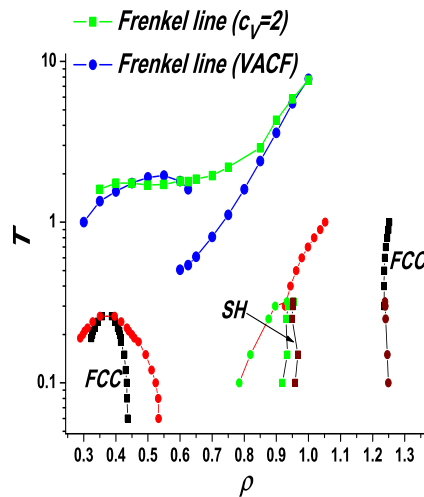


FIG. 6: (Color online) Frenkel line of the system 2 placed in the phase diagram.

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